STATICALLY AND DYNAMICALLY STABLE LITHIUM-SULFUR BATTERIES

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OVERVIEW

Timeline

- Project start date: October 2015
- Project end date: September 2018
- 20 % complete

Budget

- Total project funding
  - DOE: $ 990K
- Funding for FY15
  - $ 330K
- Funding for FY16
  - $ 330K

Barriers

- Barriers
  - Cost
  - Energy and power densities
  - Cycle life
  - Safety
- Targets
  - High-capacity, high-loading sulfur cathodes with high energy density, long cycle life, and low self-discharge

Partners

- None officially

RELEVANCE

Overall Project Objective

- Develop statically and dynamically stable lithium-sulfur batteries
  - Develop a polysulfide (PS)-filter-coated separator
  - Develop Li-S batteries with high sulfur content and loading
  - Optimize and develop advanced cell designs

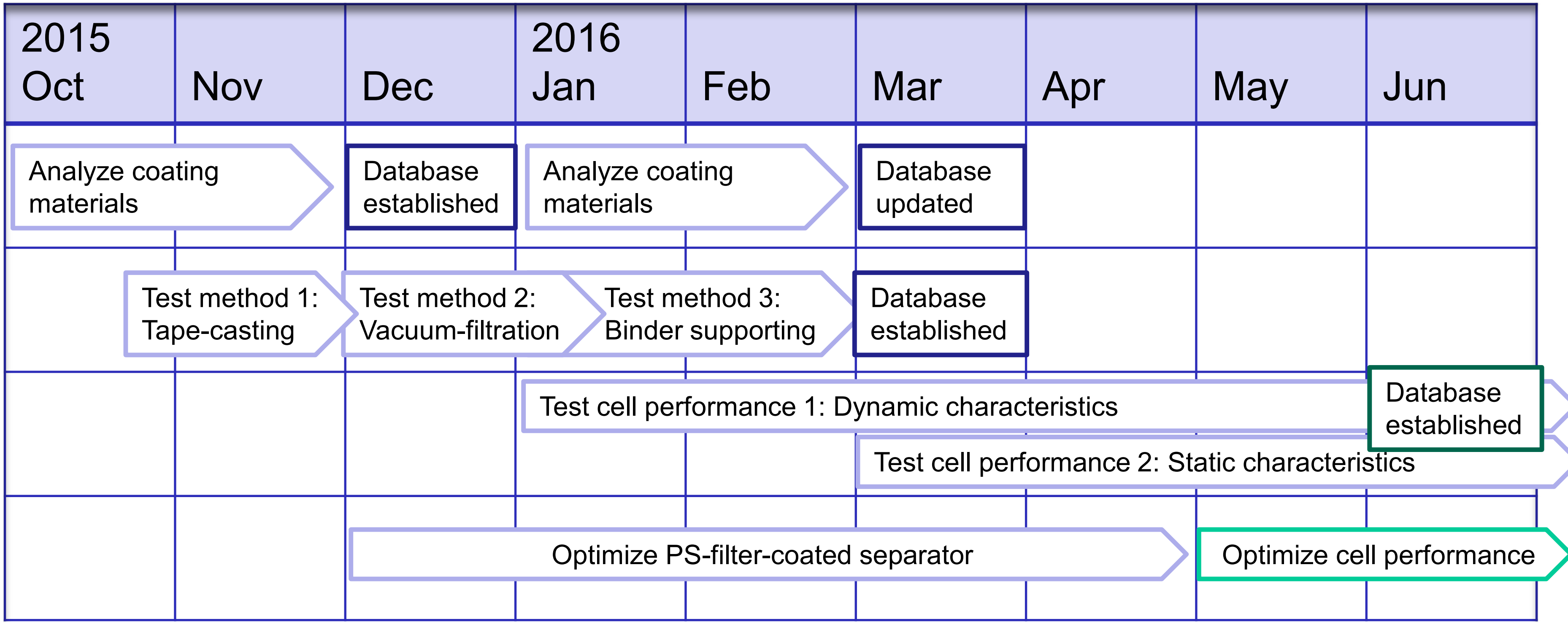
Objectives for Year 1

- Develop the PS-filter-coated separator with better electrochemical and engineering characteristics to enhance the electrochemical utilization and stability of sulfur cathodes
  - Establish materials chemistry database for the coating materials
  - Establish fabrication database for the PS-filter-coated separator
  - Assess capacity fade and self-discharge
  - Develop lightweight-coating design and electrochemically stable cells

MILESTONES

Month/Year	Milestone	Status
December 2015	Technical: Database of coating materials and PS-filter coatings established	Completed
March 2016	Technical: Database of fabrication parameters and PS-filter-coated separators established	Completed
June 2016	Technical: Low capacity-fade rate and self-discharge testing completed	Ongoing
September 2016	Go/No-go: Lightweight design and electrochemical stability demonstrated	Ongoing

APPROACH / STRATEGY



- **Go/No-go decision**

  - The Go/No-go decision on the development of the PS-filter-coated separator has been completed, as summarized in the materials chemistry database above

  - The Go/No-go decision on the enhancement of cell performance will be made after the cell measurements and optimization are finished

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

- Various coating materials with different morphologies and microstructures have been analyzed and categorized into four areas
  - The detailed materials chemistry database developed can be used to identify the key physical/chemical characteristics for improving the electrochemical properties of sulfur cathodes
  - The optimized and newly designed fabrication methods contribute to better electrochemical performance for Li-S cells and simplify the fabrication processes

- Four different carbon materials for PS-filter coatings have been established for a thorough investigation into the morphology-architecture-performance relationships
  - Spherical carbon: demonstrate the effect of porosity and structure
  - Carbon nanofiber (CNF): demonstrate the effect of coating configuration
  - CNF, carbon nanotube (CNT), and graphene: demonstrate effect of the morphology of coating materials

MATERIALS CHEMISTRY DATA

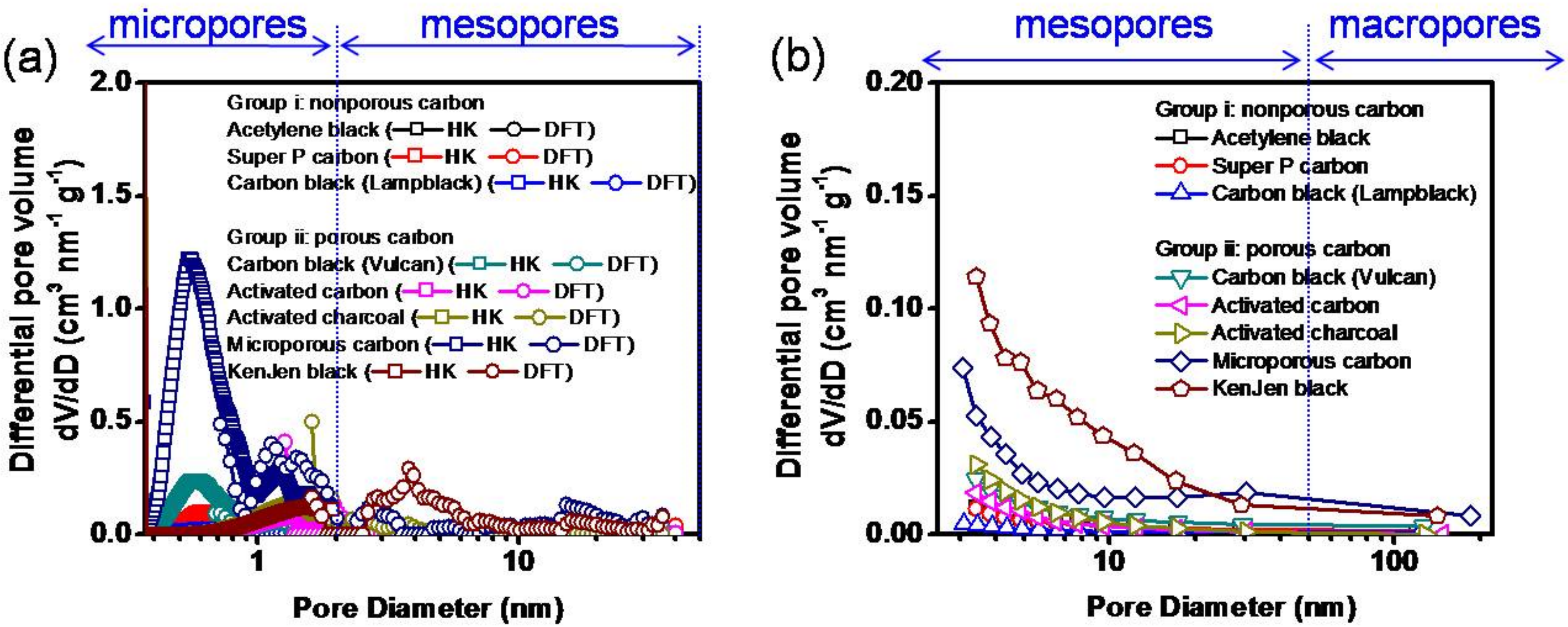
Coating material / coating methods	Carbon sample	Surface area [$m^2\ g^{-1}$]	Pore volume [$cm^3\ g^{-1}$]	Pore size [nm]	Microporosity	
					Surface area [$m^2\ g^{-1}$]	Pore volume [$cm^3\ g^{-1}$]
(i-i): T&B, V*	Acetylene Black	82	0.29	14	0	0
(i-i): T&B, V*	Super P carbon	89	0.44	19	0	0
(i-i): T&B, V*	Carbon Black (Lampblack)	30	0.22	29	0	0
(i-ii): T&B, V*	Carbon Black (Vulcan)	298	1.03	14	85	0.04
(i-ii): T&B, V*	Activated Carbon	732	0.53	3	585	0.31
(i-ii): T&B, V*	Activated Charcoal	1002	0.7	3	754	0.40
(i-ii): T&B, V*	Microporous carbon	1321	3.62	10	753	0.41
(i-ii): T&B, V*	Ken Jen black	950	2.92	12	58	0.02

Coating materials: (i) spherical carbons: (i-i) nonporous carbon and (i-ii) porous carbon
Coating methods: (T) tape-casting, (B) binder-supporting, and (V*) vacuum-filtration process with carbon nanotube (CNT) as the framework

- Group (i) spherical carbons include (i-i) nonporous and (i-ii) porous structures
- The selected spherical carbons with different porous structures and microporosity are used to investigate the key parameters for trapping polysulfides and enhancing the electrochemical reversibility

MATERIALS CHEMISTRY DATA

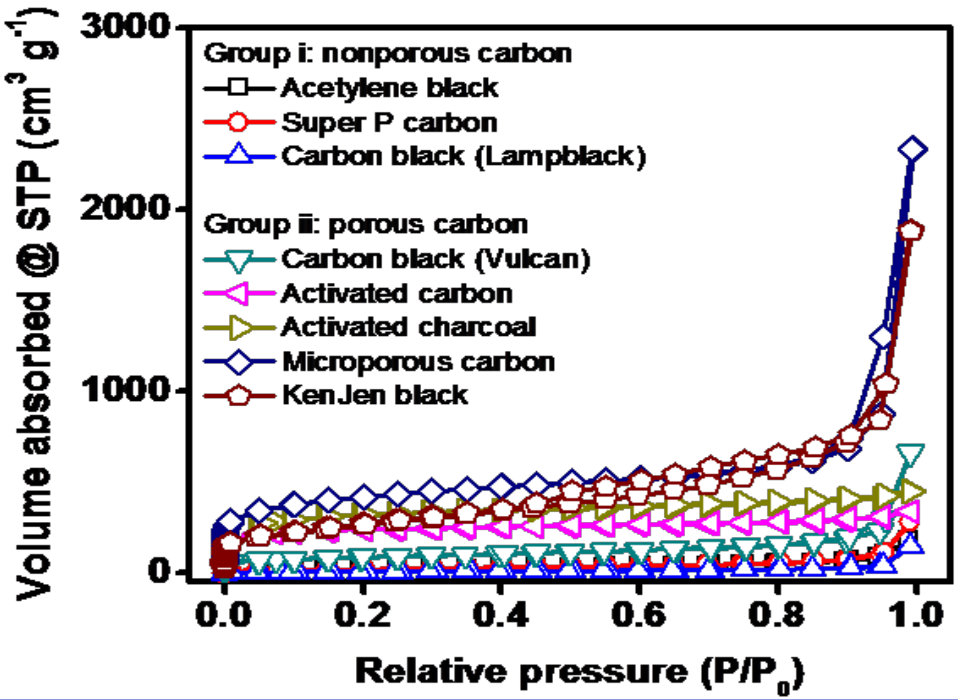
Spherical carbon: (a) HK-DFT and (b) BJH pore-size distributions



- **Horvath-Kawazoe (HK) method:** micropore distribution analysis (detected pore size (diameter): 3 – 300 nm)
- **Density functional theory (DFT) model**: micro- and meso-pore distribution (detected pore size (diameter): 0.7 – 35 nm)
- **Barrett-Joyner-Halenda (BJH) method**: broad pore-size distributions from meso- to macro-pores (detected pore size (diameter): 3 – 300 nm)

MATERIALS CHEMISTRY DATA

Spherical carbon: nitrogen adsorption-desorption isotherms



- Nitrogen adsorption-desorption isotherms showing:
  - porosity
  - porous architectures
  - micro-, meso-, and macro-pore adsorption/desorption behavior

- **Nonporous conductive carbon:** Acetylene black, Super P, Lampblack
- **High surface-area porous carbon**: Activated carbon, Activated charcoal, MPC, KJ black
- **High pore-volume porous carbon**: MPC, KJ black
- **Porous carbon with micropores**: Activated carbon, Activated charcoal, MPC
- **Porous carbon with mesopores**: KJ black
- **Porous carbon with macropores**: Vulcan black, MPC, KJ black

MATERIALS CHEMISTRY DATA

Coating material and coating method	Carbon sample	Surface area [$m^2 g^{-1}$]	Pore volume [$cm^3 g^{-1}$]	Pore size [nm]	Microporosity	
					Surface area [$m^2 g^{-1}$]	Pore volume [$cm^3 g^{-1}$]
(ii): T&B, V, V&B	CNF	26	0.09	14	0	0
(iii): V	CNT	279	2.48	36	0	0
(iv): T, B, V	RGO	272	0.57	8	11	0.003
(iv): T, B, V	EOGO	251	0.43	7	36	0.017

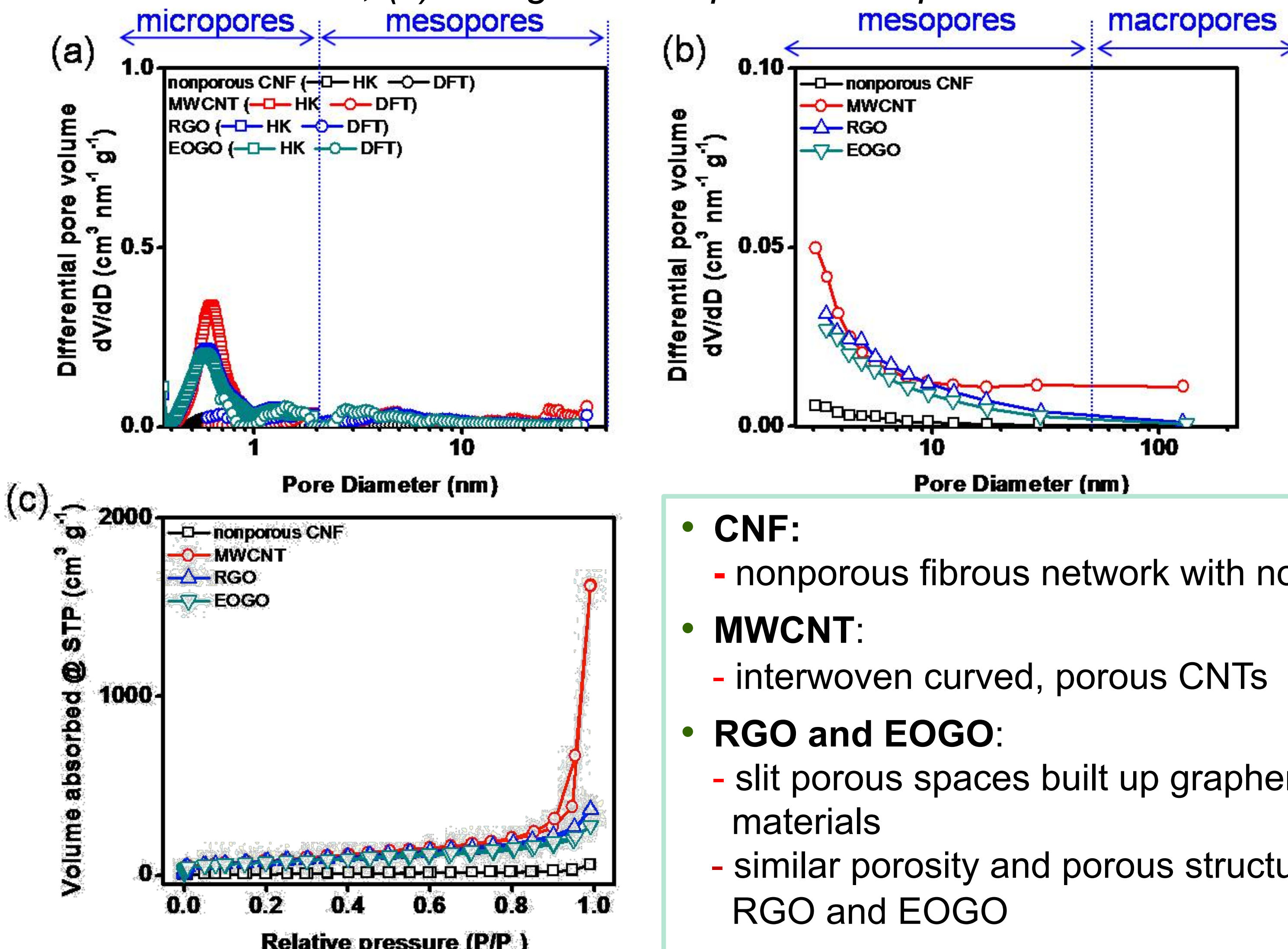
Coating materials:
(ii) carbon nanofibers (CNF)
(iii) carbon nanotubes (CNT)
(iv) graphene: edge-oxidized graphene oxide (EOGO) and reduced graphene oxide (RGO)

Coating methods: tape-casting (T), binder-supporting (B), or vacuum-filtration process (V)

- **CNF:** nonporous fibrous network
- **MWCNT**: porous tubular carbon matrix
- **RGO and EOGO**: porous flaky graphene clusters

MATERIALS CHEMISTRY DATA

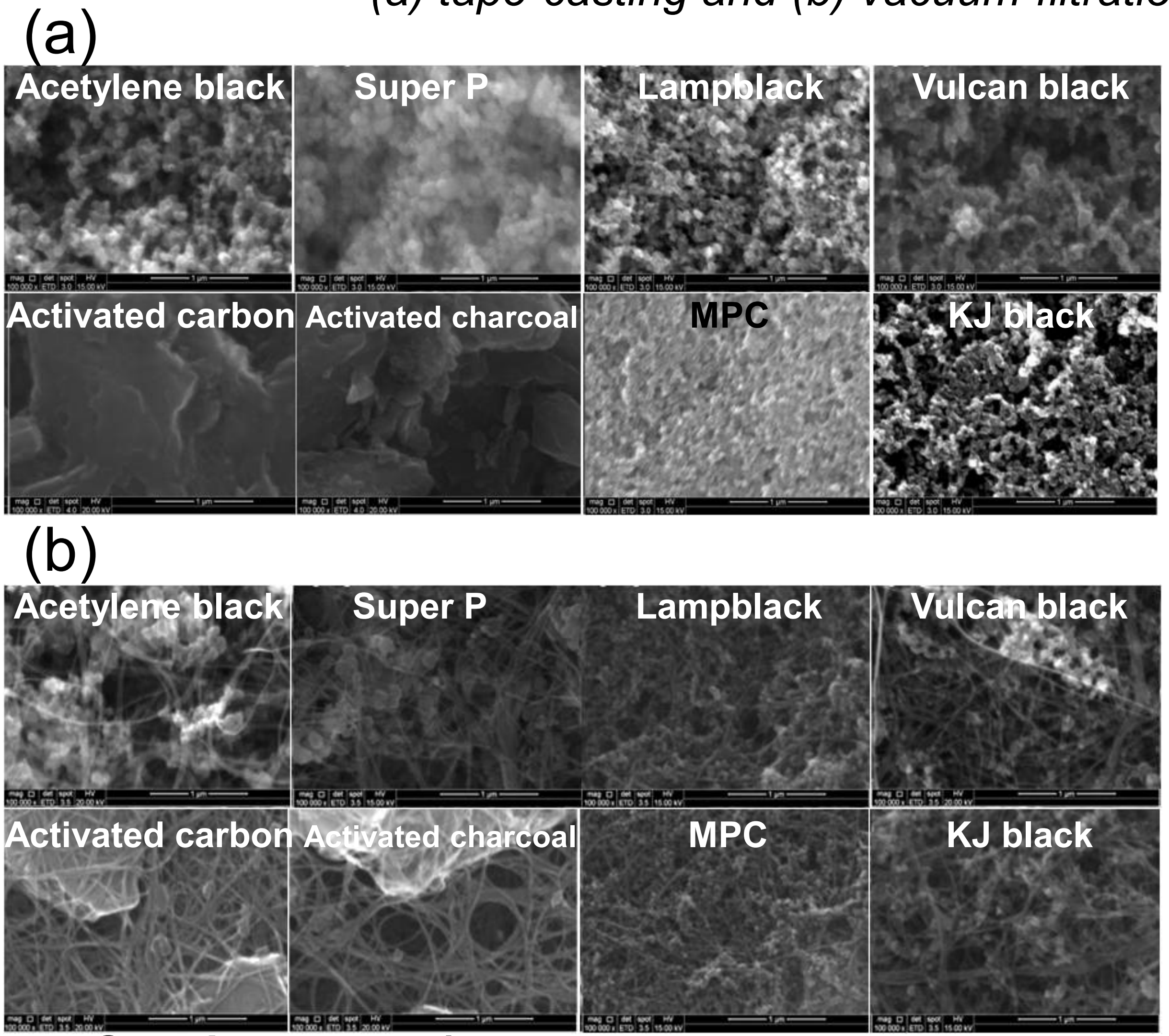
Carbon materials with various morphologies: (a) HK-DFT and (b) BJH pore-size distributions; (c) nitrogen adsorption-desorption isotherms



- **CNF:**
  - nonporous fibrous network with no pores
- **MWCNT**:
  - interwoven curved, porous CNTs
- **RGO and EOGO**:
  - slit porous spaces built up graphene-based materials
  - similar porosity and porous structure for RGO and EOGO

GROUP I: SPHERICAL CARBON MATERIALS

Morphological observation of carbon-coated separators:
(a) tape-casting and (b) vacuum-filtration methods

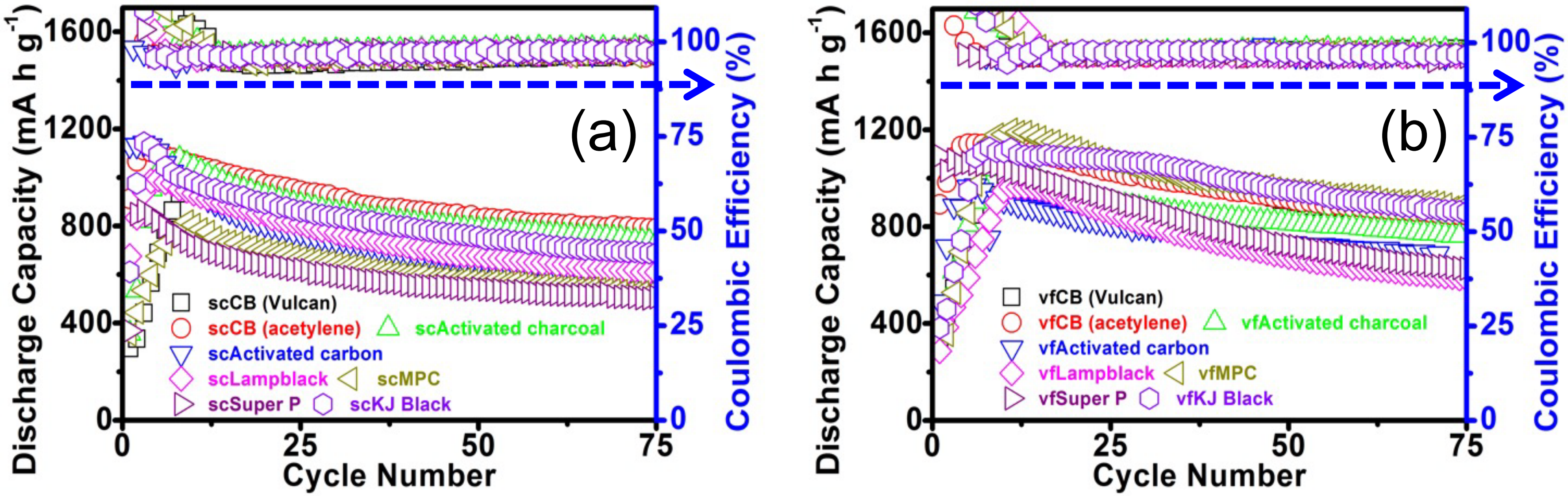


Scar bar: —— 1 μm

- Carbon materials with various morphologies and microstructures could be coated onto the Celgard membrane
- Tape-casting process is supported with polyvinylidene fluoride (PVDF) binder
- Vacuum-filtration process is supported with carbon nanotube framework
- Conductive CNT network entangles the spherical carbon in its porous spaces

GROUP I: SPHERICAL CARBON MATERIALS

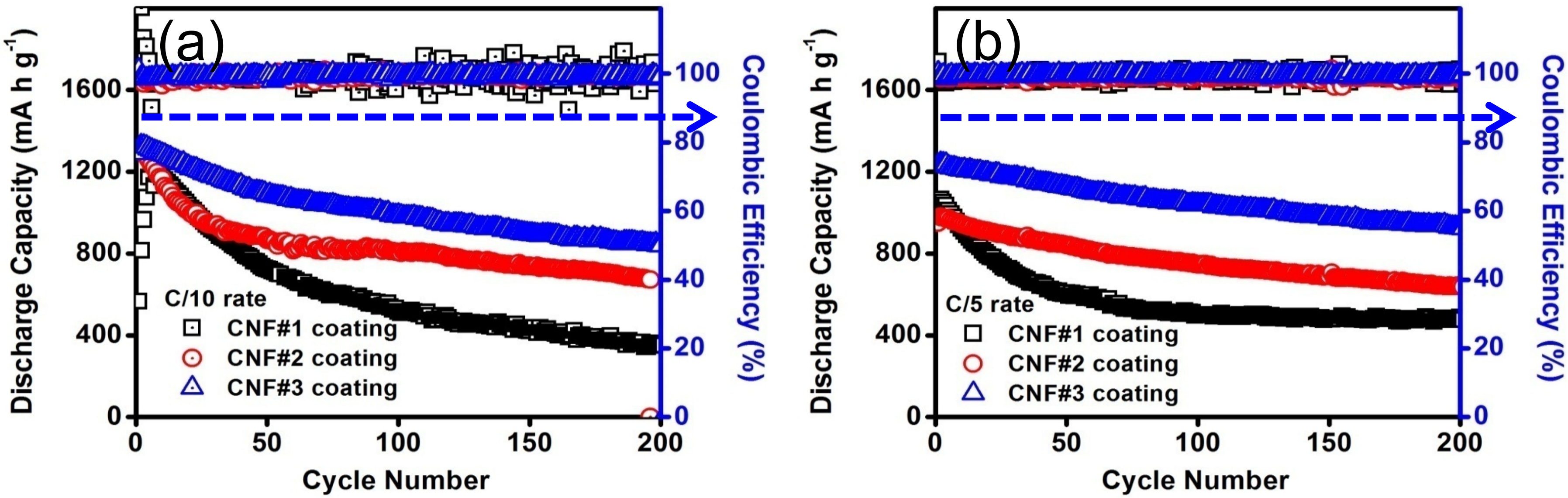
Li-S cell performance with carbon-coated separators:
(a) tape-casting and (b) vacuum-filtration methods



- PS-filter-coated separators with spherical-carbon coatings are fabricated via (a) tape-casting and (b) vacuum-filtration
- PS-filter-coated separators fabricated from the vacuum-filtration method exhibit better electrochemical performance
- Porous carbons with high surface area and pore volume (*e.g.*, MPC, KJ Black) show better cell performance and reach the targeted specific and areal capacities of, respectively, 1000 mA h g^{-1} and 4 mA h cm^{-2}

GROUP II: CNF CONFIGURATION

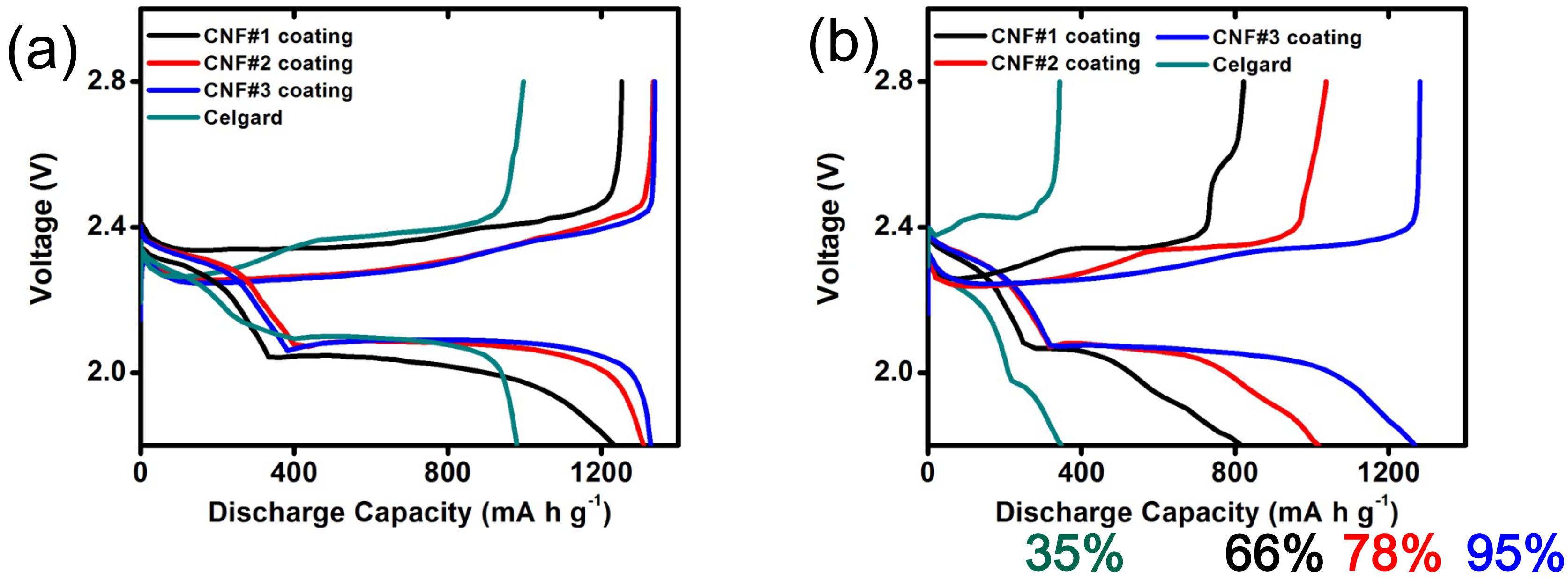
Li-S cell performance with LBL-CNF-coated separators at (a) C/10 and (b) C/5 rates



- Nonporous CNFs with low surface area and pore volume display enhanced electrochemical performance based on layer-by-layer (LBL) coating configurations with adjustable thicknesses (#1: 0.15 mg cm^{-2}; #2: 0.40 mg cm^{-2}; #3: 1.10 mg cm^{-2})
- The LBL-CNF coating boosts cell performance
  - High discharge capacity, electrochemical utilization, and areal capacity attain the targeted values of, respectively, 1000 mA h g^{-1}, 80 %, and 4.0 mA h cm^{-2}
  - Dynamic electrochemical stability achieves a low capacity fading rate of 0.1 % per cycle for 200 cycles

GROUP II: CNF CONFIGURATION

Li-S cell self-discharge measurements with LBL-CNF-coated separator: cells (a) before and (b) after resting for 15 days



- The self-discharge observation for control cell:
  - Shrinkage of upper discharge plateau: sulfur-to-polysulfide dissolution
  - Shrinkage of lower discharge plateau: re-deposition of the dissolved polysulfides
  - Increase in polarization: insulating deposits on the electrode surface

- LBL-CNF coating reduces self-discharge
  - High retention rate of the original capacity (up to 95 %) after resting for 15 days

Response to Reviewer Comments

This is a new project started in October 2015, so there are no previous reviewers comments.

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- Dr. Gabriel Veith, Oak Ridge National Laboratory

Thin-film deposition of air-sensitive sulfide materials for Li-ion battery with Li_2S-based cathodes

- pure Li_2S cathode
- Li_2S-coated cathodes
- ionic-conducting thin films (*e.g.*, Li_2S-P_2S_5)
- composite thin films (Li_2S and a conductive material)

REMAINING CHALLENGES AND BARRIERS

- **Challenge/Barrier 1:**
  The challenge to achieve the targeted areal capacity in Technical Milestone III is the development and use of high-loading sulfur cathodes. As the amount of insulating sulfur increases, the increasing cell resistance will result in low electrochemical utilization and fast capacity fade. This barrier needs to be overcome for realizing advanced cells with high energy density.

- **Challenge/Barrier 2:**
  The challenge to achieve the static electrochemical stability of Li-S battery chemistry in Technical Milestone III is the time-consuming experimental processes. Moreover, the solution to self-discharge may be challenging.

PROPOSED FUTURE WORK

- FY2016
  - To address Challenge/Barrier 1: The optimal coating configuration will improve the redox accessibility of the high-loading cathodes. Our preliminary results have evidenced the initial success of using the LBL coating and the porous carbon coating
  - To address Challenge/Barrier 2: The investigation and experiments related to the static electrochemical stability has been launched in advance. The stability is being monitored by time-dependent electrochemical impedance spectroscopy (EIS) and open circuit voltage (OCV) measurements
  - (Q3 Jun-16) Technical Milestone III: Low capacity fade rate and self-discharge testing completed
  - (Q4 Sep-16) Go/No-go: Lightweight design and electrochemical stability demonstrated

- FY2017
  - (Q5 Dec-16) Technical Milestone I: Dynamic electrochemical performance
  - This project will extend the coating materials to various metal-sulfides for investigating more detailed materials chemistry on (i) trapping polysulfides, (ii) contributing additional capacity as a co-active material, or (iii) functioning as a cathode material in Li-ions batteries
  - This project will design and develop customized cathode configurations for the development of high-loading cathodes and for the establishment of pouch-cell battery study

SUMMARY

- Systematic structural and porosity characterizations provide comprehensive materials chemistry database of various coating materials

- Materials chemistry database and the corresponding fabrication methods benefit the extended studies on the PS-filter-coated separators

  - porosity: spherical carbon with various surface areas and pore volumes
  - pore size: spherical carbon with micro-, meso-, and macro-porosity
  - configuration: nonporous CNF
  - morphology: spherical carbon, CNF, CNT, and graphene
  - modified coating method: binder-supporting, CNT-skeleton supporting

- Preliminary result for Technical Milestone III attains the targeted specific capacity (1000 mA h g^{-1}sulfur) and areal capacity (4.0 mA h cm^{-2})

  - cathodes with a high sulfur loading (3.0 mg cm^{-2}) and content (70 wt.%)
  - pure sulfur cathode with commercial micro-sized particles